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A KINETIC STUDY OF CONSECUTIVE SECOND ORDER REACTIONS

ESTER CLEAVAGES WITH HYDROBROMIC ACID

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Abstract—A study of the cleavages of diesters by HBr in glacial acetic acid reveals some interesting features. Diester cleavages are consecutive second order reactions. The reaction is accelerated by the electron withdrawing groups in the acid component and electron releasing groups in the alcohol component and it proceeds by alkyl oxygen fission (A_{AL^1}). When the medium is changed to a partially aqueous system there is a change in mechanism to acyl oxygen fission (A_{AC^2}). The change in mechanism is attributed to a difference in nucleophilicity of H_2O and the Br^- ion. The role of solvent is also discussed with reference to non-aqueous solvent mixtures.

INTRODUCTION

RESULTS of the reaction of HBr with monohydric alcohols, diols and cyclic alcohols in glacial acetic acid were recently reported.[1-3] The cleavage reactions of esters by HBr have been investigated and the cleavage of diesters in acetic acid are presented in this communication.

EXPERIMENTAL

Materials. All the substrates used were of guaranteed quality from Fluka or purified by the usual procedure and redistilled before use. The glacial AcOH used was purified by the usual procedure and distilled before use. The HBr was an azeotropic mixture distilled before use (b.p. 126°). The b.ps and m.ps of the materials used are given below:

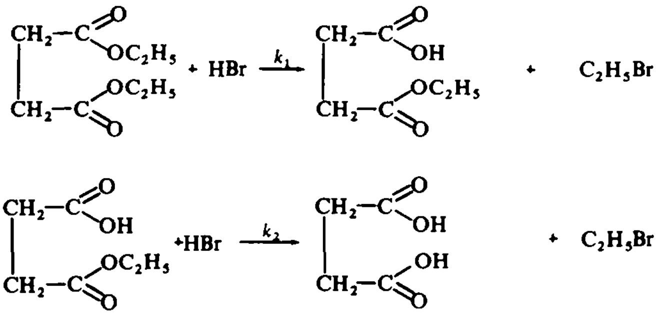
Acetic acid 118·1°; Ethyl formate 54·0°; Diethyl succinate 217·8°; Ethyl acetate 77·0°; Dimethyl succinate 195·0°; Ethyl propionate 98·1°; Dimethyl phthalate 282·0°; Ethyl benzoate 212·5°; Diethyl phthalate 299·0°; Diethyl oxalate 185·0°; Di-n-butyl phthalate 338·0°; Diethyl malonate 197·0°; Dicyclohexyl phthalate 60·2°.*

* melting point

Kinetic method: The kinetics were followed by the usual argentimetric procedure i.e. Volhard's method.

RESULTS AND DISCUSSION

The reactions are consecutive second order reactions. Plots of 1/a-x *vs* t gave two different straight lines as exemplified by the graph (Fig. 1). The values thus computed are in fair agreement with those calculated by Frost-Schwemer treatment.[4] The cleavages of esters may be represented as follows:



Frost-Schwemer treatment has been used. Values of α for duplicate runs were plotted against time on a large sheet of paper. From the resulting smooth curve the times for fixed percentages of completion were determined. Time ratios were then calculated from the times for these percentages. With the use of Frost-Schwemer Tables and these time ratios, values of $1/k$ (defined as k_1/k_2) were obtained for the reaction. The average $1/k$ value was calculated and used to obtain τ values at the various selected values of α. From the definition of $\tau(\tau = B_0k_1t)$, values of k_1 were calculated. As the $1/k$ values were below 2, Svirbely's extension was used.[5] The rates are given in Table 1.

TABLE 1. SECOND ORDER RATE CONSTANTS ($\times 10^3$ l.moles^{-1} min^{-1}) FOR THE FIRST AND SECOND STEP CLEAVAGES OF DIESTERS BY HBr AT 80°C IN GLACIAL ACETIC ACID (100%)

	k_1	k_2	k_1/k_2
Diethyl oxalate	4·766	6·666	0·7134
Diethyl malonate	6·273	12·120	0·5176
Dimethyl succinate	15·010	26·860	0·5589
Diethyl succinate	4·445	8·330	0·5337
Dimethyl phthalate	7·716	15·470	0·4990
Diethyl phthalate	2·912	5·343	0·5451
Di-n-butyl phthalate	2·380	4·948	0·4809
Dicyclohexyl phthalate	3·030	4·745	0·6384

In these consecutive second order reactions, the first step is slower and the second step relatively faster. We postulate that electron attracting groups in the acid component and the electron releasing groups in the alcohol component are accelerating, which is the diagnostic test for alkyl oxygen fission ($A_{AL}2$). The products are alkyl bromides and the acids in all the cases. It is interesting to compare the activity of the aliphatic diesters by invoking the distance between the carbethoxy groups (r) evaluated on the basis of the electrical field theory of substituent effects.[6] The rate constants of the first step of ethyl oxalate, ethyl malonate and ethyl succinate seem to exactly parallel their relative distances (*r*).

	k_1^*	r
Diethyl oxalate	4·766	3·85
Diethyl malonate	6·273	1·85
Diethyl succinate	4·445	5·85

* first step rate constants in l. moles^{-1} min^{-1} $\times 10^3$

Cleavage reaction was done with ethyl esters of formic acid, acetic acid, propionic acid and benzoic acid for purposes of comparison with the first step of oxalate, malonate, succinate and phthalate. A glance at the Table 2 makes it clear that the introduction of carbethoxy group accelerates the reaction.

TABLE 2. COMPARATIVE STATEMENT OF SECOND ORDER RATE CONSTANTS ($k_1 \times 10^3$ l.moles^{-1} min^{-1}) OF ESTER CLEAVAGES BY HBr AT 80°C IN 100% GLACIAL ACETIC ACID

	k		k_1^*
Ethyl formate	3·311	Diethyl oxalate	4·766
Ethyl acetate	5·862	Diethyl malonate	6·273
Ethyl propionate	2·526	Diethyl succinate	4·445
Ethyl benzoate	2·268	Diethyl phthalate	2·912

* rate constant for the first step

The second step is invariably high in all the cases as the reaction is controlled by the carboxyl which is adjacent and has less electron attracting power (σ values for $-COOC_2H_5$ and $-COOH$, namely $+0{\cdot}52$ and $+0{\cdot}26$, respectively, make it clear[7, 8]).

The medium of glacial acetic acid is a low polar one. Evidence has been presented[9] to show that ion pairing occurs in low dielectric media. As the mechanism in both the cases is the same, the difference in reaction rates in both the steps of all the diesters is due to the difference in formation of ion pairs or larger ion clusters in low dielectric media. Thus both the steps of each diester reaction would be to a large extent between more similar aggregates leading to values of rate constants approaching each other. As mentioned earlier the slight difference in the two steps is due to the adjacent —COOEt in the first step and the —COOH in the second step.

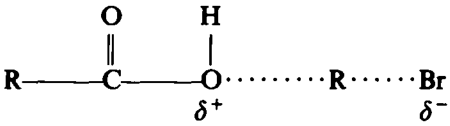
Change in solvent medium from pure acetic acid to mixed solvents like acetic acid-carbon tetrachloride, acetic acid-benzene, acetic acid-nitrobenzene and acetic acid-toluene seems to have notable effect on the process (Table 3).

TABLE 3. SECOND ORDER RATE CONSTANTS ($k \times 10^3$ l.moles^{-1} min^{-1}) FOR DIETHYL MALONATE AT 80°C IN MIXED SOLVENTS

Solvent	k_1	k_2
100% Acetic acid	6·273	12·12
70% Acetic acid–30% nitrobenzene (v/v)	5·383	10·60
70% Acetic acid–30% Carbon tetrachloride (v/v)	16·260	34·79
70% Acetic acid–30% benzene (v/v)	7·000	7·000
70% Acetic acid–30% toluene (v/v)	30·500	30·500

As the results show, in acetic acid-carbon tetrachloride or acetic acid-nitrobenzene media, the ratio of k_1/k_2 is constant, but there is a nearly three fold increase in both the steps of carbon tetrachloride mixture, whereas there is a decreasing trend of both the steps in nitrobenzene mixture. But in mixed solvents acetic acid-benzene and acetic acid-toluene, there is a significant departure. The ratio of k_1/k_2 is unity. It is seen that in the case of toluene mixture there is a five fold increase of the first step but the tendency for increase is not so pronounced for the second step, whereas, in the case of benzene mixture, there is an increasing trend in the first step and a certain retardation in the second step.

A comment on the mechanism postulated is pertinent. A plot of log *k* ester-HBr cleavages *vs* log *k* SN2 Substitution of alkyl halides seems to fit in very well, indicating similarity in mechanism. The mechanism is that of an SN2 process involving alkyl oxygen fission and the attack is on the saturated alkyl carbon, the leaving group being the acid component. The transition state in the alkyl oxygen cleavages may be pictured as:



$$R-\overset{\overset{O}{\|}}{C}-\underset{\delta^+}{\overset{\overset{H}{|}}{O}}\cdots\cdots\cdots R\cdots\cdots \underset{\delta^-}{Br}$$

In non-aqueous systems, the reaction occurs with ease. Change in solvent composition tending to an aqueous medium (50% water, 60% water v/v) leads to an interesting observation. The HBr concentration remains constant and there is no longer any alkyl oxygen fission. It changes to the acyl oxygen cleavage, usual acid catalysed hydrolysis of the ester, leaving acid and alcohol ($A_{AC}2$). The probable reason for the significant change in mechanism may be that, in a partially aqueous system, in the competition between H_2O and Br^-, water is a better nucleophile than Br^- and hence attacks the polarised carbonyl carbon forming the usual addition intermediate which breaks down to yield the products.[10] As long as the system is non-aqueous, the alkyl oxygen cleavage continues, Br^- being effective to cleave the conjugate acid formed at the ethereal oxygen in a SN2 manner.

The use of the equation,

$$k_1/k_2 = 2e^{\varepsilon^2/Drkt}$$

leads to meaningless values in low dielectric media, demonstrating the inadequacy of Ingold equation[11] as a general equation.

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